CYANIDE SOURCES

From: "Uva, Tom" <tuva@narrabay.com>
Subject: RE: Cyanide Sources

We had a similar situation with our leading newspaper about ten years ago. The paper published a full section Sunday insert detailing how they changed their production processes to eliminate solvents and switched to water based inks. It was touted in the newspaper as being revolutionary, good for the environment, could be washed down the drain and would allow color printing.

Needless to say the newspaper never notified us that they were changing their operations, unless you count the article as notification. We inspected their new plant the following day and found high levels of cyanides contained in many water based printing inks and the cyanide were not listed on the MSDS since the concentration was below the reportable levels. Typically these cyanide based inks also contain metals. The yellow and blue colors had the highest cyanide concentrations. Hope this helps you. Good luck.

PS: When you read the newspaper, I do not recommend licking your fingers to help turn the pages.

Tom Uva, Pretreatment Manager
Narragansett Bay Commission, Providence RI
(401)222-3738

From: "Bruce Wiser" <ashipp@bright.net>
Subject: RE: Cyanide Sources

I agree with Tom's answer to the cyanide question. We have a large flexographic (water-based ink) printing facility in our city. The blue inks tended to have high copper and some CN. There hasn't been a problem since they installed pretreatment.

Bruce Wiser, Assist. Dir. Of Water
Wastewater Facilities, City of Ashland
(419) 289 1392

From: "Tom Spalding" <spalding@msdlouky.org>
Subject: RE: Cyanide Sources

Careful, we have a pigment manufacturing operation in town. there is nitrate in one of the formulations. it gives a false positive for cyanide.

Tom Spalding, Lou Jeff Co MSD
502-540-6472

From: IWPPy@aol.com
Subject: Re:Cyanide Sources and Test Method Validation

It is unlikely a true cyanide compound is in the inks or glue, or the manufacturers would have run into this problem beforehand. Does the MSDS indicate any present?

An expensive ($200?) option is to verify the original test results. There are three analytical ways to validate the test method results,

Assuming the results are well above MDL.

1. Have the lab run the test using full strength sample and then using half and quarter strength dilutions. A true cyanide will give the same 'original sample' results; a false positive will likely give differing 'original sample' results.

Also, 2. Spike the full strength and quarter strength test aliquots. A true cyanide will yield at the least a linear response to both spikes (though not necessarily at the same response rate as standard cyanide solutions). A false positive will not likely yield a linear recovery response.
[First, ask your lab manager if he(she) agrees with the above rational]

A third option is to run the test using a different test method. Different results (or 'not detected') will indicate a false positive in the first test method. A true cyanide should yield fairly equivalent sample results.

Results that indicate a non-cyanide false positive can be communicated to your approval authority -- then they should agree with you that you and the IU do not have a cyanide problem.

Steve Durchin, Editor of "Industrial Waste Pretreatment Primer"

From: "Gardner, David" <GARDNER@ci.rocky-mount.nc.us>
Subject: RE: Cyanide Generation

We had an industry some time ago that was experiencing cyanide violations, but was not using cyanide in their process. They told us that they determined that the cyanide was coming in on parts that were being manufactured in South America and being processed and washed in house.

David Gardner. Supt. of Technical Services
Dept. of Water Resources, City of Rocky Mount, NC
gardner@ci.rocky-mount.nc.us

From: "Ruede, Richard" <richard.ruede@lakelandgov.net>
Subject: RE: Cyanide in Ink

We had a cardboard mfg. that used a Cupric Cyanide based ink in their process. They have since switched to a soy based products. You may want to see if you are getting Copper along with the Cyanide.

Richard J. Ruede, Industrial Pretreatment Coordinator
City of Lakeland, Water Utilities Department, 1825 Glendale Street, Lakeland, FL 33803
Phone: (863) 834-8277 Fax: (863) 834-6271
richard.ruede@lakelandgov.net

Date: Mon, 15 Oct 2001 14:02:17 -0000
From: lbruning@ci.tulsa.ok.us
Subject: Re: Cyanide in Ink

<jpridgen@w...> wrote:
"...I received several excellent responses. The biggest thing I got was that high cyanide hits had occurred from blue and yellow water based inks. My SIU is not getting much help from ink manufacturers. They state they don't have cyanide, but of course most have no lab analysis results for verification of that statement."

The blue and yellow inks sound like good places to start. A couple of careers ago, in the sixties, I was doing some drafting and seem to remember that the pigments that made "blueprints" blue were potassium/iron cyanides ("Prussian Blue" and "Turnbulls' Blue" were the two shades, as I remember) and that ferric and ferrous cyanides were lemon yellow and red pigments (Sorry, I can't remember which was- and still are-which). I vaguely recall that other metallic-cyano-complexes are also common pigmenting agents in inks, paints and pottery glazes.

I'm not surprised that manufacturers conveniently overlook these basic pigment components. We often find MSDS's that sort of lump metals, or priority pollutant organics into a catch- all phrase like "... and other inert components..."
Hope this helps.

Leo Bruning, City of Tulsa

Date: Wed, 17 Oct 2001 08:29:55 -0400
From: Jim Gwyn <jim.gwyn@ci.high-point.nc.us>
Subject: Re: Cyanide sources

Surprisingly, table salt is my first suspect. Take a look at the labels of the salt in the supermarket. You will find that a simple majority of the brands list as their second ingredient "yellow prussate of soda". This is also known as sodium ferrocyanide. It is an anticaking agent. According to a MSDS I have from Akzo-Nobel for their Diamond Crystal (R) salt that lists a maximum of 13 ppm of yellow prussate of soda.

Sodium ferrocyanide passes through the body according to the literature I've seen. However, it is most certainly broken down in the CN test. Also, we have seen numerous false positives for CN in wastewater matrices. If you want more detail, give me a holler. This is a bugbear that we in NC have been fighting for over a decade.

Jim Gwyn, Industrial Waste Supervisor
City of High Point NC
336-883-3410

Date: Wed, 17 Oct 2001 11:23:37 EDT
From: IWPPy@aol.com
Subject: Re: Cyanide sources

I have a theory about possible sources, but need some POTWs to do the homework to verify if there may be some truth in this theory. One possible source may be in photodeveloping solutions (a possible residential source), some which contain Ferricyanides.

A second possible source may be in "Alodine" (registered trade name formulations) of certain chromate-conversion baths used in metal finishing. These too contain ferricyanides.

I request any POTWs who are experiencing the reported presence of low levels of Cyanide ("Total" and/or "Amenable") in effluent, and possibly not reported in influent samples, to review their records for potential industrial sources of Alodine in their systems.

My theory will be described in the THIRD QUARTER 2001 issue of INDUSTRIAL WASTE PRETREATMENT PRIMER, and current subscribers with this problem may consider if it is worth investigating. (3rd Quarter to be released at end of October)

Otherwise, all POTWs with Cyanide effluent concerns are requested to investigate Alodine sources, and I would appreciate any feedback from those who do.

I hope this may lead to some mitigation, Steve Durchin, publisher of IWPP

Date: Thu, 25 Oct 2001 15:52:46 -0400
From: "Bruce Wiser" <ashipp@bright.net>
Subject: RE: Cyanide in Ink

I agree with your comments on the blue colored inks having CN in them. You will probably also see this with the green inks too. We have a large flexographic (water-based inks) printer in our city and I found similar CN prior to their pretreatment. This facility also does a lot of corrugation at this cardboard printing facility. I'm not sure if this would also be a source of CN or not as pretreatment seems to have solved the problem for us.

Bruce Wiser, Dir. of Water/Wastewater Facilities, City of Ashland, OH

We've had these same POTW effluent results for years. There seems to be a holding time problem with the analysis--if it is run the same day as the sample is taken, there is no violation. If the sample is held more than 24-hours (which is okay by Standard Methods) we get a hit in the effluent. Our chemist discovered this years ago, and has since run cyanide in-house and reports those results. It is very consistent that if he runs a sample and holds a sample, the "held" sample has higher CN, or if it goes to a commercial lab and is run later, the CN is higher. Don't know why.

Gayle Tupper, Hayward
gaylet@ci.hayward.ca.us

Date: Wed, 20 Nov 2002 09:29:48 -0600
From: "Lee Davis" <ldavis@mail.ci.dallas.tx.us>
Subject: Re: Cyanide Source Control - response

we had a similar problem with a company that produced printed drinking cups. we found that some of the inks contained thiocyanates which showed up as cyanide when doing the total cyanide test. try testing for amenable cyanide to see if there is really free cyanide in the effluent of the company in question.

metal finishers that use metabisulfate to reduce hexavalent chrome can also have false positives for total cyanide. apparently through some weird chemistry the metabisulfate also produces a thiocyanate compound which again shows up in the total cyanide.

finally as steve noted inks can be a real problem for metal depending on the formulation. copper being the main culprit (blues and greens). your best bet is to make sure anyone doing a lot of printing with colored inks capture any excess and dispose of it somewhere besides the sewer.

Lee Davis, REM
Dallas Water Utilities, Pretreatment and Lab Services
phone: 214 243-2367
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mailto:ldavis@mail.ci.dallas.tx.us

Date: Wed, 20 Nov 2002 09:01:43 -0700
From: RHogrefe@cabq.gov
Subject: Re: Re: Cyanide Source Control - response

Other than electroplaters who use large vats with CN and precious metals, we have found jewelers using strong cyanide and hydrogen peroxide solutions to descale finished jewelry silver pieces in a process they call "bombing" and is highly dangerous, although the finish is superior and they have a hard time not using it, the spent solutions are often poured down the drain, we have found 5 gallon buckets to be the usual quantities. We have converted this practice in some instances to less dangerous techniques without CN by emphasizing the safety hazards they are exposing their workers to. Others still use it and have learned to destroy the spent solutions with bleach treatment and letting the buckets just sit around for a month until it is oxidized to cyanate that is less toxic, but can still be picked in total CN tests.

Some CIU's are regulated under CN tests as amenable to chlorine which may not pick up the cyanates, still other tests detect just the free forms (so called weak acid dissociable test) that is thought to be the most appropriate measure of active cyanide and excludes much of the otherwise combined forms of cyanides and interferences that continue to plague all CN testing. A new Lachat Micro Dist test method is showing promise and has been ok'd by EPA Office of Water for total CN testing for NPDES permittees. You can learn a lot about CN testing from the Lachat company, see www.lachatinstruments.com

Also, Hach has new methods and kits people are using that are microdistillation based, and Hach always has a wealth of information. We have found the key is to get a lab to counter as many of the potential interferences in whatever CN test, Standard Methods has them listed for reference, it has been our best guidance.

Date: Wed, 20 Nov 2002 13:12:57 -0500
From: "Stephen Miller" <smiller@sd1.org>
Subject: RE: Cyanide Source Control

Cyan blue (Prussian blue) is used as an anti clumping agent in road salt (thus blue color) not certain, but think it is used in some inks

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Date: Wed, 20 Nov 2002 15:29:40 -0500
From: "Jim Gwyn" <jim.gwyn@ci.high-point.nc.us>
Subject: RE: Cyanide Source Control

Has anyone implemented source control for cyanide, or cyanide-containing or -forming compounds?

Has anyone found a particular problem industry (possibly unpermitted ones) in terms of cyanide contribution to the influent?

As was noted elsewhere, sodium ferrocyanide (aka yellow prussate of soda) breaks down to yield HCN in the cyanide acid distillation. Sodium ferrocyanide is used to the extent of about 5 ppm in table and much industrial salt as an anti caking agent. I have seen sodium ferrocyanide listed many times on the ingredient lists for salt used in textile mills.

I also have an aluminum diecaster that seems to generate cyanide in their process. All they do is to melt aluminum alloys and inject them into molds. Apparently, the aluminum reacts with nitrogen from the air and carbon to produce cyanides. I've heard that this is an issue in the primary production of aluminum by the Hall process.

Jim Gwyn, Industrial Waste Supervisor, City of High Point, NC
336-883-3410.

Date: Tue, 26 Nov 2002 08:24:18 -0500
From: "Uva, Tom" <tuva@narrabay.com>

Subject: RE: Re: Cyanide Source Control - resp onse

Cyanides are also formed in the air scrubbers at POTWs that incinerate sludge. We have also recently discovered that road salt used for deicing contains ferri-cyainde. Cyanide is also in the water based printers inks.

Tom Uva, Narragansett Bay Commission, Providence, RI

Date: Tue, 26 Nov 2002 08:42:30 –0500
From: kfe <kfe@bactapur.com>
Subject: Re: Re: Cyanide Source Control - response

Cyanides, at low concentrations, are readily biodegradable, by certain bacteria. Optimization of sludge digestion can reduce volume and digest cyanide. Ferrocyanide is a free running agent added to salt. I believe it is even in table salt.

Karl F. Ehrlich, Ph.D.
Bacta-Pur®, New Bedford, MA

Date: Tue, 26 Nov 2002 15:49:07 -0800
From: "Jeff Macfarlane" <jmacfarlane@ndsd.org>
Subject: Re: Re: Cyanide Source Control - response

Ferrocyanide is also in the red fire retardant used to fight forest fires. It doesn't seem to have any negative effects on the environment even when it is spread all over the mountainside.

Jeff Macfarlane
IPP, NDSD, Syracuse, Utah

Date: Fri, 13 Jun 2003 12:58:19 -0500
From: "Lee Davis" <ldavis@mail.ci.dallas.tx.us>
Subject: Re: Cyanide in Pipeline

we have seen bogus cyanide results in waste water where sodium bisulfite is used to reduce hex chrome to tri chrome. our former lab supervisor explained the chemistry to me which i promptly forgot. however the short version is that the bisulfite morphs into some sort of cyanate which then shows up after the sample digestion as CN. ask someone in your lab to research it.

peace,

Lee Davis, REM
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Date: Mon, 16 Jun 2003 11:30:37 EDT
From: IWPPy@aol.com
Subject: Re: Cyanide in Pipeline

There is a possibility of chemical impurity even in purchased reagent-grade products, and greater chances as the purity of the purchased chemical or substance decreases in quality. I have even observed Arsenic listed as a trace impurity in bagged iron sulfate used at water treatment plants. So consider checking for presence of trace cyanide salt in the Bisulfite by having the lab run a true reagent blank against a reagent blank using the same strength bisulfite solution used at your sampling point. PPBs in PPMs are a 1/1000 ratio, so if the reagent manufacturer was running a cyanide batch just prior to running bisulfite...?

Steve Durchin, publisher of "Industrial Waste Pretreatment Primer"

Date: Thu, 11 Sep 2003 15:11:20 -0000
From: "jothaler_ftch" <jothaler@ftch.com>
Subject: Re: cyanide analysis

FYI, the Michigan is changing the analytical testing requirement for cyanide from Method 335.1 to Method OIA-1667 (see http://www.epa.gov/waterscience/methods/cyanide/).

The Michigan water quality standard regulates "free cyanide" and 335.1 has long been used to measure amenable cyanide as a surrogate for free cyanide and various cyano-complexes that may dissociate upon discharge to surface waters. They now believe OIA-1667 is superior as to lower detection limit (2 ug/L vs. 5 ug/L), better accuracy and precision, as well as elimination of potential interferences from substances other than cyanide that can react in the chlorination step.

My experience with OIA-1667 is that it can show interference by sulfides, so the lab needs to know if they are present so appropriate precautions can be taken. I also understand that OIA-1667 does not perform as well for samples that contain high concentrations of nickel, mercury, or silver cyanide complexes. In addition, not all labs currently offer OIA-1667.

Jerald O. Thaler, P.E.
Fishbeck Thompson Carr & Huber
Farmington Hills, MI

Re: Cyanide

Posted by: "Heil, Ann" aheil@lacsd.org annthei l
Wed Dec 20, 2006 8:44 am (PST)

Our agency has found that excessive concentrations of cyanide (greater than 5 ug/L) are formed when we conduct free/breakpoint chlorination. When we do chloramination (as we currently do at all of water reclamation plants), cyanide concentrations are below discharge standards. However, with chloramination, if we preserve our cyanide samples to pH >12, then we get false positives for cyanide. Cyanide is created in the preservation process. We worked around this problem by doing immediate analysis of cyanide with no preservation at all of our WRPs.

Ann Heil, LACSD

Date: Mon, 18 Aug 2003 14:20:39 -0700 (PDT)
From: John Michael <vanya189@yahoo.com>
Subject: Re: Cn Interferences

I have seen Cn form from from wet scrubbers as a result of incomplete combustion, but it's usually in HCN form. Do they have a scrubber for their off gases from their lab hoods? Do they combust the off gases? That could be a souce. And if there's a carbon source it's easy to scavenge N from the air when there's low thermal settings when the oxygen has been consumed freeing up Nitrogen to combine with Carbon. When this occurs CO is usally visible in the lab hood vents. So if they report CO in the air emissions then look for the CN if there's a wet scrubber.

JOHN M. SALONICH

Re: Nitrifying Trickle Filter - Nitrification Inhibition
Posted by: "John Michael" vanya189@yahoo.com vanya189
Wed Feb 9, 2011 12:51 pm (PST)

Several years ago we did some work for a large CT WWTP that had similar issues and they discovered that the source of inhibition was coming from their "scrubber" cooling water post incineration of their sludge where HCN was forming.

HCN is a known inhibitor to nitrification. Does your treatment plant operate or accept cooling water of a scrubber from a sludge incinerator? It could be temperature related by incomplete destrtionof the off gases.

John Salonich
